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Hydrodesulfurization NiMo catalysts supported on Co, Ni and B modified Al_2O_3 from Anderson heteropolymolybdates

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Abstract

Recent catalysts of hydrodesulfurization (HDS) reaction consist of CoMo and NiMo phase supported on gamma-Al_2O_3 support. The support was modified with cobalt nitrate, nickel nitrate, or boric acid and high loadings of Anderson type heteropolyoxomolybdate $(NH_4)_3[Ni(OH)_6Mo_6O_{18}].7H_2O$ were deposited. Surface area (S_{BET}) and sulfide phase dispersion of the catalysts were determined by N_2 physisorption and O_2 chemisorption, respectively. Samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, infrared and UV-Vis spectrometry, and temperature programmed reduction. The activity of catalyst was measured in HDS of 1-benzothiophene. The preliminary incorporation of Co, Ni and B into the support increased the HDS activity of the deposited NiMo phase. IR and UV-Vis DR data revealed the partial decomposition of the initial Anderson type NiMo complex with a formation of new surface compounds, including heteropolymolybdates and separated polymeric oxomolybdenum compounds. X-ray photoelectron spectroscopy showed that the degree of Mo sulfidation is the smallest for the catalysts prepared over unmodified alumina and boron-modified alumina. The highest degree of sulfidation was found for the catalysts supported over Co- and Ni-modified alumina. The nickel-modified alumina increased the HDS activity and dispersion of the NiMo phase the most, which was associated with the formation of the largest number of active sites.

Keywords: NiMo/γ-Al_2O_3; anderson heteropolymolybdate; additives Co, Ni, B; benzothiophene hydrodesulfurization

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1. Introduction

Sulfur compounds present in fuel generate polluting emissions. Increasingly strengthen regulations limits the sulfur content in fuels. Supported Co (Ni) molybdenum catalysts are extensively used in hydrotreating processes for the production of environmentally friendly fuels, and these catalysts have been extensively studied [1]. The nature of the support plays an important role in the morphology and dispersion of the active phases and catalytic activity of the catalysts [2]. A synergistic effect between the support and the NiMo hydrodesulfurization (HDS) catalysts has been proposed [3]. Various supports have been studied for hydrotreating catalysts. The most widely used support remains alumina because of its excellent mechanical and dispersing properties [4]. As a rule, the active components are loaded on the support using cobalt (nickel) nitrates and ammonium heptamolybdate solutions. For this catalyst, the promoting effect of Co(Ni) appears at a Co(Ni)/(Co(Ni)+Mo) ratio of 0.3-0.6 [5]. Despite intensive research over the last decade, the promoting role of Co, Ni, and the support remains unclear. Previous studies have shown that the use of heteropolyoxomolybdate in the preparation of HDS catalysts may provide an interesting alternative to traditional systems [6,7]. It has been shown [8-13] that the usage of ammonium salts (e.g., $CoMo_6O_{24}H_6$ or $NiMo_6O_{24}H_6$) gives a higher HDS activity at a lower Co(Ni)/(Co(Ni)+Mo) molar ratio (0.14). Therefore, Anderson-type heteropolycompounds are effective precursors to the multilayered active phase of hydrotreating catalysts. However, their hydrodesulfurization (HDS) and hydrogenation (HYD) activity depend on the nature of the heteroatom [14].

Various methods of catalyst modification are applied to improve the catalytic performances of the CoMo and NiMo catalysts and to elucidate the effect of the support properties on the HDS activity. Various additives can be used to modify properties of the support. Contradictory results have been reported in the literature regarding their effects on the properties of the alumina support and the HDS catalyst. For example, Li et al. [15] has found a correlation between acidity and HDS activity for the CoMo/alumina-aluminum borate catalysts. They found a beneficial effect on the acidity and metal dispersion upon addition of boron. Ramirez et al. [16] has shown that the promotional effect of boron on HDS activity reaches its maximum at 0.8 wt% B. In contrast, Perez-Martinez et al. [17] has found a decrease in HDS activity based on a study of the effect of acid-base characteristics of alumina (γ-Al_2O_3) modified with B, Na, or K used for diesel hydrotreatment. This result may be due to changes in the distribution of Co and Mo species in the oxide state. Lafitau et al. [18] observed lower interaction between loaded metals and alumina in the presence of boron. On the other hand, Houalla and Delmon revealed that the addition of boron promotes the interaction between cobalt and alumina in the CoMo/Al_2O_3 catalysts [19]. Giraldo and Centeno [20] stated that CoMo and NiMo supported on alumina modified by different quantities of B_2O_3 (4-14 wt%) did not change the HDS activity at low boron content in these catalysts. The NiMo catalysts showed slightly higher activity than the CoMo catalysts.

Recently we have shown that alumina modified with various amounts of Co prior to the deposition of cobalt heteropolyoxomolybdate up to a molar ratio of Co/Mo = 0.27 substantially increases the activity of the HDS of thiophene and 1-benzothiophene [21]. The aim of this work is to study the influence of Ni, Co or B modification of the alumina support on the properties and the HDS activity of NiMo/γ-Al_2O_3 catalysts prepared using Anderson-type Ni heteropolyoxomolybdate. The activity of the catalysts has been studied for the HDS of 1-benzothiophene.

2. Experimental

The parent NiMo catalyst has been prepared using a ground commercial γ-Al_2O_3 support (S_{BET} = 200 m^2g^{-1}, total volume of pores = 0.40 cm^3g^{-1}, average radius of the pores = 3.2 nm, particle size fraction = 0.16-0.32 mm). The support was impregnated with an aqueous solution of the ammonium salt of nickel